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CADMIUM COATINGS CONTAINING DISPERSED NICKEL
PARTICLES FOR THE PROTECTION OF HIGH STRENGTH
STEELS AGAINST CORROSION

G. Sanderson, et al

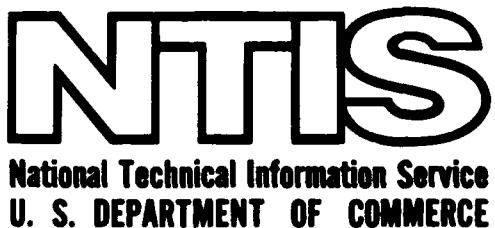
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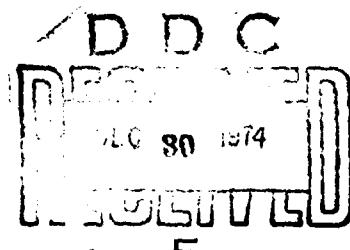
PROCUREMENT EXECUTIVE,MINISTRY OF DEFENCE
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**Cadmium Coatings Containing
Dispersed Nickel Particles
for the Protection of
High Strength Steels
Against Corrosion**

by
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FULMER RESEARCH INSTITUTE LTD.

JULY 1974

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Electrodeposited Cadmium Coatings Containing Dispersed Nickel Particles
for the Protection of High Strength Steels Against Corrosion

by

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Fulmer Research Institute Ltd.

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Foreword

This report is a summary of work carried out by Fulmer Research Institute Ltd., under Ministry of Defence Contract K43A/141/CB43A2. The work was supervised by Mat. NF4 under the direction of ADRMat2/NF.

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ELECTRODEPOSITED CADMIUM COATINGS CONTAINING
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HIGH STRENGTH STEELS AGAINST CORROSION

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SUMMARY

Slow strain rate and sustained load tensile tests on 300M and NCMV alloys have shown that the susceptibility of these high strength steels to hydrogen embrittlement during plating with cadmium, can be considerably reduced in both as-deposited and baked conditions by co-depositing nickel particles with the cadmium. The nickel particles are thought to preferentially absorb hydrogen both during plating and in the post-plate baking treatment.

The corrosion resistance of Cd/Ni composite coated steel panels in outdoor exposure tests appears to be better than simple cadmium-plated steel panels under the same conditions.

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CONTENTS

	<u>Page</u>
SUMMARY	c
1. INTRODUCTION	2
2. EXPERIMENTAL PROCEDURES	2
2.1. Optimisation of the dispersion of nickel particles in aqueous media when agitated by a plate pumper unit.	2
2.2. Preparation and testing of composite cadmium-nickel coated test specimens.	3
2.2.1. Determination of % nickel incorporated in cadmium plate under various operating conditions.	3
2.2.2. Assessment of corrosion resistance of the composite coatings by exposure testing at Fulmer.	4
2.2.3. Susceptibility to hydrogen embrittlement	4
2.2.3.1. Slow Strain rate tests	5
2.2.3.2. Sustained load tests	5
3. EXPERIMENTAL RESULTS	5
3.1. Effect of cell parameters on the uniformity of dispersion of powder in a plate pumping cell	5
3.2. Effect of operating conditions on % Ni incorporated in cadmium electroplate.	6
3.3. Corrosion resistance of coated mild steel panels in exposure tests at Fulmer.	6
3.3.1. Appearance on plating	6
3.3.2. Appearance after exposure	7
3.4. Slow strain rate tests	7
3.5. Sustained load tests	7
4. DISCUSSION OF TEST RESULTS	7
5. CONCLUSIONS	9
6. REFERENCE	11
TABLES	12 - 15
FIGURE 1.	16

1. INTRODUCTION

The work described below summarises the research carried out on the assessment of electrodeposited cadmium coatings containing hydrogen absorbent dispersed nickel particles as a possible coating system for giving corrosion protection to high strength steels, whilst ensuring minimum susceptibility to hydrogen embrittlement.

The research consisted of the following main sections:-

1. Optimisation of the powder dispersion characteristics of a nickel powder slurry agitated in a cadmium plating solution by a plate pumping technique.
2. Determination of factors controlling the amount of nickel co-deposited with cadmium in this system.
3. Assessment of the corrosion resistance of composite coated steel panels exposed to the atmosphere at Fulmer Research Institute.
4. Assessment of the susceptibility of two high strength steels coated with cadmium-nickel composite deposits to hydrogen embrittlement failure by slow strain rate and sustained load tensile tests.

2. EXPERIMENTAL PROCEDURES

2.1. Optimisation of the dispersion of nickel particles in aqueous media when agitated with a plate pumper unit.

In order to keep the nickel particles in suspension in the cadmium cyanide plating solution, it is necessary to agitate the solution. Preliminary work was carried out in a flowing solution operated by a peristaltic pump, or in a solution through which air was bubbled, but it was found that plate pumping maintained the most uniform suspension, and this technique was used for all the work described here.

The apparatus - Figure 1 - consists of a rectangular poly-propylene plating cell of dimensions 20cm x 12.5cm x 28cm with a working capacity 5 - 6 litres. A tight fitting, uniformly perforated poly-propylene plate is able to oscillate vertically in the lower 3 cms of the cell interior by its supporting frame being connected to a pneumatic pump.

Plates of different perforations and different pumping rates were selected and a set of experiments carried out to determine the best operating conditions for uniform dispersion of nickel powder in

water. Sampling of the slurries was made immediately after pumping for 10 minutes by pipetting 10 ml aliquots from the top and bottom regions of the slurry volume, centrifuging and decanting the clear liquor, drying the powder and weighing to \pm 0.0001gm.

The nickel powder, nominally 1 μm average diameter, was size classified by gravity settling to narrow the experimental size range to 90% within 0.1 - 1.0 μm . Ball milling in water was found to be satisfactory in breaking down agglomerates to the desired unit sizes before sizing.

The dispersion experiments were carried out using a bath loading of 50gm nickel powder per litre of water.

2.2. Preparation and testing of composite cadmium - nickel coated test specimens

2.2.1. Determination of % nickel incorporated in cadmium plate under various operating conditions

All cadmium plating was carried out to Ministry specification D.T.D. 904 in a cyanide bath of Canning "Zonax" salts made up to the manufacturer's instructions, and using the optimum pumping plate predicted from the data of 2.1. above.

Square section rod specimens of N.C.M.V. alloy of dimensions 0.5cm x 0.5cm x 5cm were plated in duplicate with cadmium-nickel coatings under various operation conditions selected from the following levels of operating parameters:-

Concentration of Ni powder in bath - 50, 200 g/l

Current Density - 50, 100, 200 A/m²

Agitation rate - 40, 80 cycles/min.

Plating time - 60 mins.

Powder treatment - mixed with cadmium solution by light ball milling, wetting agent added to the bath (0.1 ml of Lissapol N to 5 litres of cadmium solution).

The specimens were pre-treated by vapour degreasing in trichloroethylene, weighed to 0.0001 gm, anodically electrocleaned in a proprietary alkaline cleaner, washed in tap water and distilled water, then lowered into the middle of a cylindrical cadmium anode in the cadmium-nickel bath with the voltage applied.

After the specified plating time the specimens were washed well in tap water to remove loosely adhering particles, dried and

weighed. The coatings were dissolved in hot hydrochloric acid and the nickel content determined by precipitation as the dimethylglyoxine complex.

2.2.2. Assessment of corrosion resistance of the composite coatings by exposure testing at Fulmer

Mild steel panels (0.1m x 0.15m) were pre-treated as above and coated on both sides with cadmium or composite cadmium-nickel deposits to 25 μm in the plate pumper cell. A constant agitation rate of 40 cycles/min and constant nickel concentration of 50 gm/l, where applicable, were used throughout.

In an attempt to produce smoother deposits, and because it has been suggested¹ that most hydrogen present in a cadmium coating exists near the interface of steel and cadmium, some panels were treated with cadmium-nickel to 8 μm followed by cadmium to 25 μm total thickness.

Cadmium and cadmium-nickel plus cadmium deposits were formed at 100 A/m² whereas cadmium-nickel coatings were produced at 50 A/m², again to minimise nodular growth.

Half the panels coated were given a passivation treatment after plating according to D.E.F. 130 by immersing for up to 10 secs. in a sodium dichromate and sulphuric acid mixture followed by rapid rinsing. Half the total panels were scored to the steel through the coatings. The following panels, in duplicate, were then fastened with plastic nuts, bolts and washers to an exposure frame in the Institute grounds facing north and inclined at an angle of 45°:-

- (a) Plain Cd, Cd/Ni, Cd/Ni + Cd.
- (b) Passivated Cd, Cd/Ni, Cd/Ni + Cd.
- (c) Scored Cd, Cd/Ni, Cd/Ni + Cd.
- (d) Scored passivated Cd, Cd/Ni, Cd/Ni + Cd.

Visual examination of the panels was carried out at intervals from November 1972 to August 1973. Emission of acid fumes from a chemical laboratory close to the site leads to a reasonable simulation of an industrial atmosphere at the site.

2.2.3. Susceptibility to hydrogen embrittlement

Two tests have been used to estimate the effect of the nickel particles on the susceptibility of cadmium plated high strength steels to hydrogen embrittlement.

- (i) Slow Strain rate tensile tests - rapid.
- (ii) Sustained load tensile tests - long term.

2.2.3.1. Slow Strain rate tests

Duplicate plain specimens of 300 M and N.C.M.V. steels with gauge length 1.95×10^{-2} m, diameter 0.32×10^{-2} m were plated after masking the screw threads, with Cd, Cd/Ni and Cd/Ni + Cd as above in a bath containing 50 gm Ni/litre at an agitation rate of 40 cycles/min. and current density of 100 A/m^2 to a thickness of $25\mu\text{m}$. The specimens were washed and dried and half of them subjected to a 24 hour baking treatment at 200°C .

The slow strain rate tests were conducted at room temperature and a crosshead speed of 6.548×10^{-8} m/sec. Measurements were taken for each specimen of % elongation, maximum stress, reduction of area of cross section of the gauge length, and time to failure.

2.2.3.2. Sustained load tests

Notched tensile specimens of N.C.M.V. and 300M alloys had a 2.54×10^{-2} m gauge length, 0.454×10^{-2} m gauge length diameter, containing a 90° notch giving an overall notched diameter of 4.064×10^{-2} m. The notched tensile strength of each alloy was determined before any samples were plated and tested.

The specimens were plated as above with Cd, Cd/Ni, or Cd/Ni + Cd. The screw threads of each test piece were then plated with $25\mu\text{m}$ of cadmium to minimise loss of hydrogen from the ends while under the lengthy tests. Half the specimens were baked as above.

The specimens were loaded in proving rings to 75% N.T.S. and the time to failure recorded.

3. EXPERIMENTAL RESULTS

3.1. Effect of cell parameters on the uniformity of dispersion of powder in a plate pumping cell

The concentrations of nickel powder obtained in 10 ml aliquots of top and bottom volumes of slurry are given in Table 1 with the test conditions. Clearly, the optimum dispersion conditions would achieve top and bottom concentrations of 0.5 gm/10ml and a concentration ratio of unity.

3.2. Effect of operating conditions on % Ni incorporated in cadmium electroplate

The weight percents nickel obtained in cadmium electroplates formed under various operating conditions are given in Table 2.

Regression analysis of the data with no impressed boundary conditions e.g. if concentration of Ni in the bath = 0, %Ni in the deposit = 0, gave the following best fit:-

$$\begin{aligned} \% \text{Ni} &= (0.35 \pm 0.87) + (0.00016 \pm 0.00005) \text{Ni}_{\text{bath}} \times j \\ &+ (0.0003 \pm 0.0001) \text{Ni}_{\text{bath}} \times A \\ (\text{d.f. } 2, 9) F &= 17.3 \text{ with } 79.3\% \text{ of the experimental variance explained.} \end{aligned}$$

By setting the boundary condition - when $\text{Ni}_{\text{bath}} = 0$, $\text{Ni}_{\text{deposit}} = 0$, in order to eliminate the dubious constant term, the following gave the best fit:-

$$\begin{aligned} \% \text{Ni} &= (0.00017 \pm 0.00005) \text{Ni}_{\text{bath}} \times j + (0.0004 \pm 0.0001) \text{Ni}_{\text{bath deposit}} \times A \\ (\text{d.f. } 2, 10) F &= 80.7 \text{ with } 94.2\% \text{ of the experimental variance explained.} \end{aligned}$$

The presence of a wetting agent in the bath or ball milling the Ni powder before use had no apparent effect on the amount of nickel incorporated or the appearance of the plate. High current density and high agitation rates appeared to favour dark nodular deposits and in subsequent plating of test specimens, lower current densities and agitation rates have been used.

Some preliminary experiments with layered coatings - 20 minutes of composite coating followed by 40 minutes of cadmium plating at 100 A/m^2 gave considerably smoother coatings and this combination has been included in the test sequences.

3.3. Corrosion resistance of coated mild steel panels in exposure tests at Fulmer

3.3.1. Appearance on plating

On preparation the Cd/Ni deposits tended to be uniform in colour but darker and more nodular than pure Cd coatings. Overplating of ~ 8 μm of composite Cd/Ni with Cd considerably improved the appearance of the coatings.

3.3.2. Appearance after exposure

After 10 weeks' exposure one of the cadmium-scored panels showed rusting along a score mark but this had not deteriorated since first noticeable (2 weeks). Both cadmium plated specimens showed flaking of the plate and some base metal corrosion. One passivated cadmium plated specimen showed flaking of the deposit.

After 10 months' exposure the following panels showed rusting of the mild steel base:-

- (i) Both cadmium only plated specimens (1.0 and 0.3 x area of the panels).
- (ii) Both cadmium plated and passivated specimens (0.3 and 0.8 x area of the panels).
- (iii) Both cadmium plated and scored specimens (0.25 and 0.2 x area of the panels).
- (iv) One cadmium/nickel plated and scored specimen (corner of the panel).

All other panels showed no rusting of the mild steel.

Some of the composite plated panels showed local corrosion of the cadmium in the form of white pin-points.

3.4. Slow strain rate tests

The data obtained from the slow strain rate tests are given in Table 3.

3.5. Sustained load tests

The 75% NTS sustained load test results are given in Table 4.

4. DISCUSSION OF TEST RESULTS

The experiments performed to determine the cell parameters required to give optimum dispersion of nickel powder in the aqueous solution have shown that a uniform and full dispersion can be obtained at the 50 gm/litre level of loading. More recent work at Fulmer on composite plating, and the experiences of other workers, have shown that uniform dispersion in the bath, and hence in the deposit, is more consistently obtained by use of heavier bath loadings of powder viz. 200 gm/litre. With the latter, random fluctuations in process parameters do not have such a significant effect on powder dispersion.

However, experience has shown that even at 50 gm/litre powder content, the dispersion uniformity can be maintained to sufficiently consistent values to ensure practically uniform deposit powder distribution of average composition better than approximately \pm 30% of the expected value. The present investigation indicates that at 50 gm/litre loading, the standard residual differences between the observed and predicted % Ni in the deposits varies between 11 and 47% of the predicted value, whereas for 200 g/l loading the range narrows to 2-19% of the predicted values. The operating conditions selected for preparation of the test specimens are calculated to give the desired 1-2 wt % Ni in the deposits.

Both the slow strain rate and sustained load tests in air show positive correlation of reduction in hydrogen embrittlement failure with the presence of nickel powder in the cadmium plates.

In the sustained load tests - 75% NTS in air - the 300M alloy appeared to be considerably more susceptible to failure than the NCMV alloy. For 300M in the baked condition both composite coatings (Cd/Ni and Cd/Ni + Cd) gave complete protection to the steel, the specimens not failing after > 5000 hours compared to 23.9 hours for the simple cadmium plated and baked sample. In the unbaked condition all three specimens failed with the composite coatings appearing to give greater resistance than the simple cadmium plate - 71 and 45.5 hours c.f. 1.3 hours. However, it is not felt that the life times are large enough for great significance to be given to the unbaked specimen data.

NCMV seemed to exhibit considerably more natural resistance to hydrogen embrittlement failure where cadmium plated, failure occurring after 1813 and 1945 hours for as-deposited and baked conditions respectively. Specimens coated with the full composite coating, (Cd/Ni throughout), did not fail after 5857 and 5461 hours respectively. 8 μm of Cd/Ni overplated with 16 μm of cadmium did not improve the test life compared with cadmium plate.

Examination of the reduction of area of cross-section of the slow strain rate specimens after test reveals some significant trends. With 300M, considerable embrittlement occurs when plated with cadmium in both the as-deposited and baked conditions (<6% R. of A. compared with 25% as-received alloy). Both types of composite coating significantly reduced embrittlement, the reductions of area experienced on fracture being >20%, in the case of completely Cd/Ni deposits approaching 30%.

Similar trends were observed with the NCMV alloy. The 16% R. of A. measured for the as-received steel is probably lower than the actual value; unfortunately, lack of further available specimens prevented a repeat test. In each condition, as-deposited and baked, both types of composite coating appeared to reduce the embrittlement found on cadmium plating, yielding increased R. of A's, e.g. 2% Cd as-deposited, 15% Cd/Ni as deposited, 10% Cd/Ni + Cd as deposited.

Exposure tests on coated mild steel panels from November 1972 to August 1973 showed that the composite coatings successfully prevented corrosion of the mild steel. Localised attack in the form of small white spots was probably due to cadmium corrosion set up by cadmium-nickel galvanic couples.

The mechanism by which co-deposited nickel particles reduce hydrogen embrittlement in cadmium plated high strength steels has not been investigated. However, it is thought that the nickel preferentially absorbs hydrogen produced during plating - supported by the as-deposited slow strain rate and sustained load tests - and by preferential absorption and desorption away from the steel-coating interface aids removal of hydrogen from the steel during baking - indicated by the baked specimen tests.

5. CONCLUSIONS

1. Nickel particles can successfully be incorporated in cadmium electrodeposits on steels by co-deposition from an electrolyte-nickel slurry.
2. Sustained load and slow strain rate tensile tests in air show a positive correlation between reduction in susceptibility to hydrogen embrittlement failure of cadmium plated high strength steels, and the presence of 1 to 2% of 1µm nickel particles in the cadmium deposits.
3. The corrosion resistance of composite cadmium-nickel electroplated steel is at least as good as cadmium plated steel when assessed by outdoor exposure tests.
4. The method of incorporating hydrogen absorbent particles in cadmium plate by co-deposition is a novel and potentially useful way of protecting high strength steels and avoiding plating embrittlement failure. Further development and testing of plated components against other forms of cadmium plate would be required.

Note A British Patent covering the process has been granted under the title "Improvements in Electrodeposited Metal Coating" B.P. No. 1349735.

REFERENCE

1. Kudryavtsev, V.N., et al., Trans. I.M.F., 50, 223, 1972.

TABLE 1

EFFECT OF CELL PARAMETERS ON THE POWDER DISPERSION

Hole Size (cm)	Hole Spacing (cm)	Rate of Agitation (cycles/min)	Wt. Powder in lower level/10ml (gm)	Wt. Powder in upper level/10ml (gm)	Ratio
0.1	1.25	44	0.2579	0.2396	1.076
0.1	1.25	82	0.3089	0.3057	1.010
0.25	1.25	40	0.3815	0.2680	1.423
0.25	1.25	78	0.3902	0.2670	1.462
0.63	1.25	46	0.3250	0.2400	1.354
0.62	1.25	86	0.3450	0.2670	1.292
0.1	2.5	42	0.2662	0.2477	1.075
0.1	2.5	78	0.2646	0.2431	1.095
0.25	2.5	48	0.3715	0.3475	1.069
0.25	2.5	86	0.5890	0.4400	1.339
0.62	2.5	44	0.6272	0.2285	2.748
0.62	2.5	80	0.4976	0.4496	1.107
0.1	3.8	44	0.1640	0.1486	1.104
0.1	3.8	86	0.2057	0.2907	0.708
0.25	3.8	40	0.3423	0.2893	1.183
0.25	3.8	80	0.5120	0.3565	1.436
0.62	3.8	44	0.2515	0.2634	0.955
0.62	3.8	78	0.2370	0.2245	1.055

The results show that the largest hole size gives generally higher powder contents in the solution and some ratios near unity. Repeat experiments were carried out at various agitations with:

- (a) 0.62 cm holes, 2.5 cm spacing
- (b) 0.62 cm holes, 3.8 cm spacing

It was found that (a) at high agitation gave somewhat better reproducibility and high powder contents and was used in subsequent experiments where possible.

TABLE 2

EFFECT OF OPERATING CONDITIONS ON % NI CO-DEPOSITED

Test Run	Ni in Bath g/l	Current Density A/m ² (j)	Agitation Rate cycles/min. (A)	Time (mins)	Other Conditions	Wt % Ni
G	50	200	40	60	Wetting Agent	0.98
H	50	200	80	60	"	0.99
K	50	200	40	60	"	4.78
L	50	50	40	60	"	1.39
P	200	50	40	60	Pwdr.ball milled	6.17
Q	200	100	40	60	milled	5.00
R	200	200	40	60	"	10.85
S	200	100	40	60	"	5.31
T	200	100	80	60	"	9.38
U	50	200	40	60	"	3.68
W	50	100	80	60	"	3.42
X	50	200	80	60	"	5.02

TABLE 3

SLOW STRAIN RATE TEST DATA FOR NCMV AND 300 M ALLOYS

Alloy	Plate	% Elongation	Max. Stress GN/m ²	R. of A. %	Time to Failure (hours)	Heat Treatment
NCMV	As Received	6.41	1.93	16	6.75	-
		4.21	1.98	12.0	6.15	Baked
		5.15	1.93	12.0	5.3	Baked
		1.07	1.83	2.0	4.5	-
	Cd/Ni	6.21	2.09	18.0	6.6	Baked
		5.52	2.15	15.0	6.4	-
		4.77	1.98	29.0	6.5	Baked
	Cd/Ni + Cd	6.26	2.02	30.0	6.5	Baked
		4.82	-	10.0	-	-
		5.73	2.02	10.0	6.75	-
300M	As received	7.94	1.93	25.0	6.75	-
		1.14	1.74	2.0	4.0	Baked
		6.88	1.50	6.0	6.0	Baked
		3.48	1.82	5.0	5.4	-
	Cd/Ni	6.11	2.13	30.0	5.8	Baked
		7.81	2.04	29.0	6.6	-
	Cd/Ni + Cd	7.59	1.82	20.0	5.8	Baked
		6.42	1.28	25.0	5.7	Baked
		6.26	1.72	25.0	5.3	Baked

TABLE 4

SUSTAINED LOAD TEST DATA FORNCMV AND 300M ALLOYS

(75% NTS in air)

Alloy	Plate	Heat Treatment	Life (hours)
NCMV	Cd	-	1813 (F)
		Baked	1945 (F)
	Cd/Ni	-	5857 (NF)
		Baked	5461 (NF)
	Cd/Ni + Cd	-	212 (F)
		Baked	2049 (F)
300M	Cd	-	1.3 (F)
		Baked	23.9 (F)
	Cd/Ni	-	71 (F)
		Baked	5649 (NF)
	Cd/Ni + Cd	-	45.5 (F)
		Baked	4904 (NF)
NF = not failed up to quoted life F = failed at quoted life			

NCMV NTS = 2.62 GN/m²300M NTS = 2.90 GN/m²

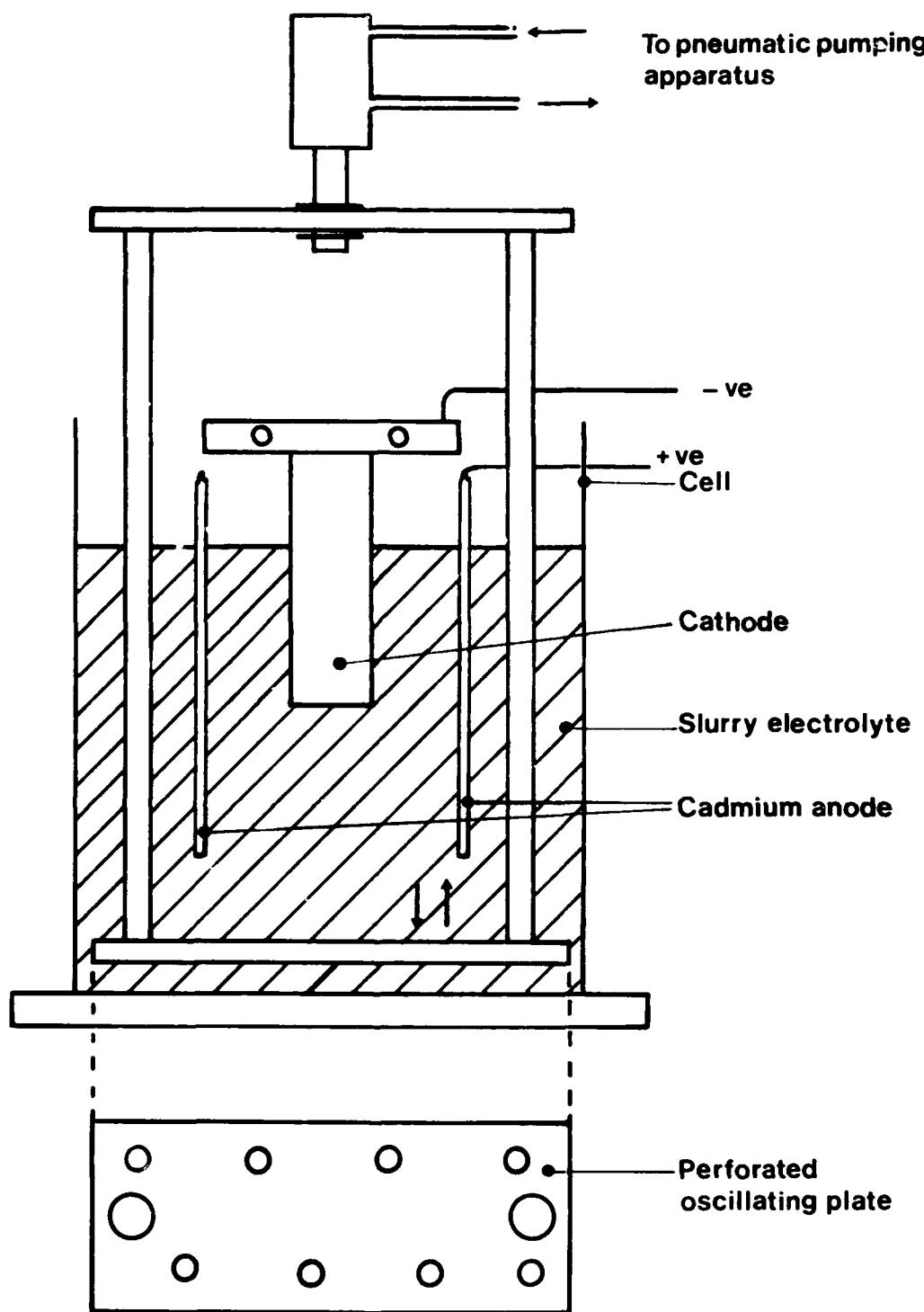


Figure 1. Slurry electrolyte apparatus showing plate pumping arrangement